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Increasing the Hydrogen Content of Aromatic Polyimides for Radiation Shielding

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Science in Chemistry from
The College of William and Mary

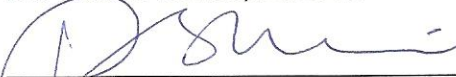
by

Geoffrey T. Geberth

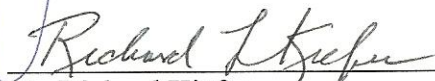
Accepted for honors



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April 30, 2014

Abstract

One of the significant problems facing space exploration is the presence of high energy radiation in this non-terrestrial environment. Significant exposure to this radiation poses a serious hazard to both the personnel and equipment during extended flights or extra-terrestrial habitation. Traditional methods used for shielding high energy radiation on Earth are not practical due to the conditions necessary for space flight. Polymers present a feasible alternative to the traditional radiation shielding methods, providing a material that can serve as both a lightweight structural component and at least one component in a shielding system that protects the crew from the deadly radiation flux in the hostile environments of space. This research focuses on two approaches to the development of a hydrogen-rich polymeric system in order to increase the hydrogen content in previously synthesized polyimides.

Acknowledgements

I would like to pay a special thanks to Dr. Robert Orwoll and Dr. Richard Kiefer. They have guided me throughout my entire undergraduate career, and their impact on my life cannot be overstated. Thank you to Dr. Kristin Wustholz and Dr. Paul Bhasin for agreeing to be a part of my committee, and for the significant roles that they have played in the past several years. Thank you to all of my friends and associates who have stood by me through all of it, and have helped me get to where I am today. I would like to acknowledge with gratitude financial support from International Scientific Technologies Inc. under NASA contract numbers NNX11CI31P, NNX11CB81C, and NNX13CL05C.

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I. Introduction

A. Particle Radiation

One of the largest threats to both personnel and equipment on extended space missions is the large amount of high energy ionized particle radiation, especially bare atomic nuclei, present in non-terrestrial environments.

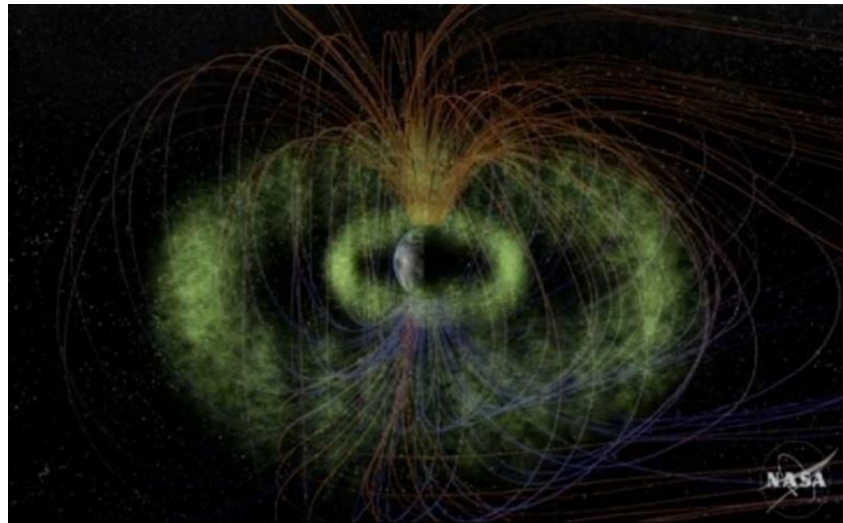


Figure 1 - The Van Allen Radiation Belts¹

The Earth's magnetic field shields the planet's surface from the bulk of this particulate radiation, trapping it in the Van Allen radiation belts (Figure 1) well before it reaches the surface of the Earth, while the atmosphere protects the planet from harmful electromagnetic radiation. Unfortunately, any voyage beyond the outermost Van Allen belt leaves a vessel unprotected. Extended exposure to this radiation can lead to adverse health effects, and, eventually death. Such effects are a result of the fact that charged-particle radiation in space has sufficient energy to pass through both tissue and shielding materials, while ionizing them. Ionization causes much more severe and complex health issues than electromagnetic radiation can cause. Particle radiation is also capable of unleashing the phenomenon known as cascading radiation. When high Z particles, such as iron nuclei, collide with a material, the nucleus can fragment into multiple charged particles. The

fragments generate more radiation behind a material than is incident to a shield, and even alter the physical properties of the shield by causing internal defects on the atomic level.^{2, 3}

In order to make a manned mission to Mars and extra-terrestrial habitation possible, and reduce risk to astronauts, it is necessary to find a means of reducing these effects. There are three primary types of particle radiation an astronaut would be exposed to that would have adverse health effects: solar radiation, charged species trapped in the Van Allen belts, and galactic cosmic radiation.

1. Solar Radiation

The sun is a very powerful source of radiation within the solar system, emitting primarily high energy protons and alpha particles (two protons and two neutrons). These particles are relatively low in energy, but have an extremely high flux (between 10^{10} and 10^{15} particles/cm²s). Fortunately, the sun's magnetic field keeps these harmful waves of radiation contained for the most part. During large solar events such as solar flares, however, large quantities of solar protons and alpha particles are ejected from the sun's magnetic field.³ These events can be catastrophic to a space mission. There is little threat from this radiation within the safety of Earth's magnetic field, but beyond this protection, the sheer quantity of radiation can be devastating if it is not properly shielded.

2. The Van Allen Radiation Belts

The Van Allen radiation belts are regions of trapped radiation located in Earth's magnetosphere. Until recently, it was believed that there were only two of these radiation belts, one ranging from approximately 1,000 km to 6,000 km above Earth, and the other ranging from approximately 15,000 to 25,000 km above Earth. These belts are comprised of both free protons

and electrons and only free electrons respectively. The recent Van Allen probes, however, have revealed the existence of a third, isolated radiation belt farther out than the other two that does not appear to always be present. The protons and electrons trapped within the radiation belts are at a higher energy than those from solar radiation, but they have a lower flux. The belts form from ions that are trapped in the magnetic field. It congregates in these regions as the magnetic field slows down the charged particles. These particles also travel down the magnetic field lines into the atmosphere, creating the auroras. Radiation belts are not a phenomenon that is unique to Earth, as several planets throughout the solar system have radiation belts. Any planet with a strong enough magnetic field can support Van Allen belts, making them a potential hazard for orbiting planets besides Earth.⁴ Radiation exposure from the Van Allen belts only represents a temporary threat to astronauts on long range missions, but still poses a hazard for any missions that stay within the confines of the Earth's magnetic field.

3. Galactic Cosmic Radiation (GCR)

The primary radiation threat in deep space is Galactic Cosmic Radiation (GCR). It is made up of the bare nuclei of every naturally occurring element, with some nuclei even travelling at near light speeds. The elemental abundances vary dramatically, however, with those elements heavier than iron being nearly negligible. Hydrogen and helium make up approximately 85 % and 14 % of GCR respectively. For lighter elements, making up about 1% of GCR, the elements with even charge numbers are much more abundant than their odd counterparts, with the most abundant species being carbon ($Z = 6$), oxygen ($Z = 8$), magnesium ($Z = 12$), silicon ($Z = 14$), and iron ($Z = 26$)³. Previously it was thought that GCR originated in super novae due to the elemental concentrations being very similar in makeup to that of the solar system and stars, but recent isotopic studies suggest that they are not the source, but merely the

means of accelerating the particles. It is, however, believed that the source lies within our galaxy, but outside of our solar system⁵. GCR is slowed by the expanded solar corona; consequently the levels of radiation fluctuate with the solar maxima and minima, with GCR being at a maximum during the solar minimum.

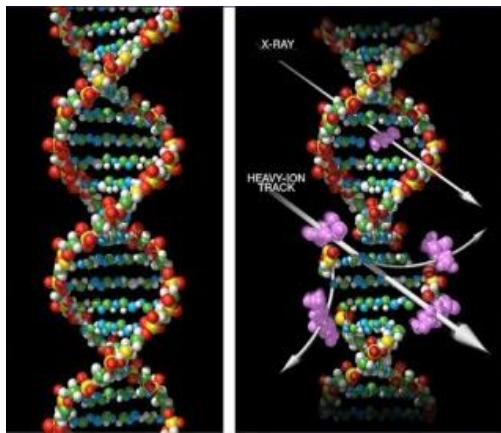


Figure 2 – Radiation Damage to DNA⁶

There is very little data concerning the biological effects of GCR exposure (as it cannot be accurately replicated on Earth), but it is clear that extended exposure can result in carcinogenesis and mutagenesis.³ The extent of the effects is a function of the mass and energy of the incident particles because of their capacity to ionize materials and tissue, leading to degradation.

B. Solution Framework

This work focuses on the development of shielding materials for the particle components of space radiation. Because these shielding materials are intended for use in space, traditional terrestrial radiation shields, such as lead and concrete, are not practical. A shield made from these materials would be too heavy to leave the launch pad. A lighter alternative is clearly necessary. GCR is susceptible to passive radiation shielding through Coulombic interactions as it consists of bare, positively charged nuclei. Materials that carry a high density of electrons should be able to slow down incident particles via ionization and excitation. With a nucleus that consists solely of a proton, hydrogen has the highest electron density (electrons per atomic mass) of any element, leading to the idea that high hydrogen content would provide an effective radiation shield. Because of the charged nature of solar radiation and the Van Allen Radiation

Belts, any material that can shield astronauts from GCR should be capable of also protecting against these additional forms of particulate radiation.

Liquid hydrogen would be an ideal material for shielding this type of radiation, but that is impractical. Water represents another potential solution. With a makeup that is 11 wt-% hydrogen and a density of 1 g/cm^3 in its liquid state, it is hydrogen rich and fairly light-weight compared to lead or concrete. Unfortunately, liquid water would be difficult to contain, and it experiences wide fluctuations in its dimensions as it freezes, and maintaining a uniform liquid shield would prove difficult. Liquid shields also cannot serve dual functions as structural elements.

Polymers present another potential solution to this problem. Their tunable properties, stability, relative strength, and easy molding make polymeric systems a very attractive alternative. Traditional hydrogen-rich polymers, such as polyethylene and polypropylene (each containing approximately .14 mol H / g polymer) do not have suitable properties for the harsh conditions that they must be able to withstand for space travel, nor do they possess the mechanical strength that would allow them to serve as structural components. Compounds such as polyimides with aromatic backbones, on the other hand, have the mechanical strength and chemical and thermal properties that are more than sufficient to survive even the harshest of environments. Several polyimides, poly-oxydiphenylene-pyromellitimide (Kapton®^{*}), for example, have already found a variety of uses on spacecraft. Unfortunately, these highly conjugated systems are relatively hydrogen deficient (.026 mol H / g Kapton®), and so do little in the way of shielding radiation. In the past, novel hydrogen rich polyimides have been synthesized in house, but there is a limit to how much hydrogen can be in a system using

^{*} See Appendix

commercially available monomers, and synthesis of novel monomers can be a very complex process.

This research focuses on using alternative methods to improve the hydrogen content of UDABAM

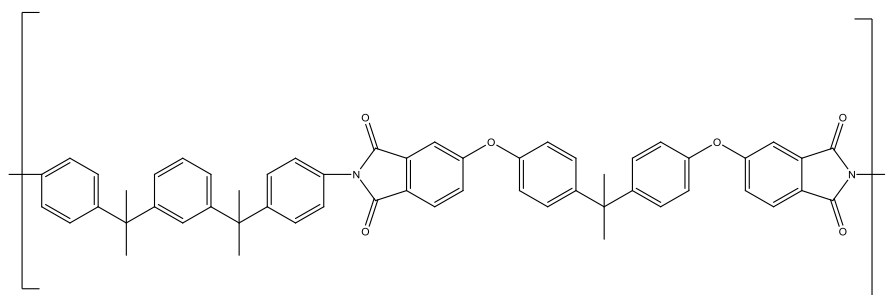


Figure 3 – UDABAM Polyimide

(Figure 3), a polyimide previously developed and synthesized in house from the commercial monomers UDA [4,4'-(4,4'-Isopropylidenedi-phenoxy)bis(phthalic anhydride)] and BAM [4,4'-(1,3-phenylenediisopropylidene) bis aniline]. With a hydrogen content of .054 mol H / g UDABAM, this polyimide contains over twice as much hydrogen as Kapton® while maintaining similar properties, however this hydrogen content is still well below those of water and polypropylene. The number of aromatic rings along the backbone, however, suggests that the hydrogen content of this polyimide could be increased post-polymerization. Aromatic substitution reactions and the synthesis of an interpenetrating polymer network system offer two potential methods to increase the hydrogen. Through synthetic means, it is not an unreasonable idea to create a high performance polymeric system that could serve as both a radiation shield and a structural component on a spacecraft or habitation that has hydrogen content comparable to that of water's .11 moles H / g H₂O. The research described here is an investigation of these two approaches to adding more hydrogen to high-performance shielding polymers.

II. Initial Research and Methods

A. Post-functionalization via Electrophilic Aromatic Substitution

1. Friedel-Crafts Alkylation Reaction

One of the main causes for the stability of these polyimide chains is the abundance of aromatic rings in the backbone. The resonance in these rings leads to improved stabilization and increased thermal and mechanical properties. The aromatic rings also offer the only sites along the polymer backbone that are available for additions of substituents with high hydrogen content.

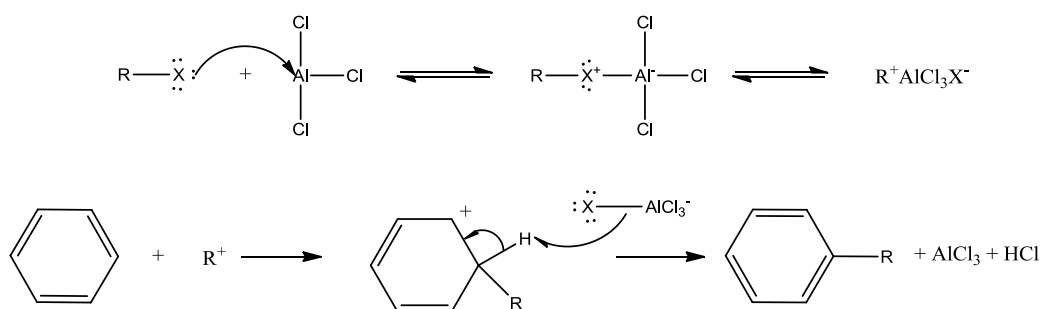


Figure 4 – Friedel-Crafts Reaction Mechanism

Only a limited number of reactions are actually available to add to these aromatic rings. These are the aromatic substitution reactions, in which a hydrogen, or a substituent, is removed from the ring and is replaced by another substituent. The Friedel-Crafts alkylation reaction is a classic example of this type of reaction. Friedel-Crafts alkylation (Figure 4) proceeds through a carbocation generated from a Lewis acid stripping the halide from an alkyl halide. The generated carbocation electrophilically attacks the electron density of the aromatic ring, generating a resonance-stabilized cation intermediate. The hydrogen from the ring transfers to the halide from the alkyl halide, restoring aromaticity, regenerating the Lewis acid, and generating a strong acid as a byproduct with the abstracted hydrogen combining with the free

halide. This research utilizes bromoethane as the alkyl halide in order to generate ethyl substituents.

In traditional organic synthesis, the Friedel-Crafts alkylation reaction is seldom used because, while it is reliable, it is very difficult to control, often leading to multiple additions when only one is desired. Multiple additions occur because the alkylated ring is more activated than the original molecule. The Friedel-Crafts acylation is usually favored over the alkylation due to the superior control that it offers, typically terminating after one substitution. Patil reports the post-functionalization of poly(isobutylene-co-p-methylstyrene) via a Friedel-Crafts acylation reaction. His work involved substitutions of a β -ketocarboxylic acid on the pendant aromatic unit of the p-methylstyrene.⁷ It would not be unreasonable to extend this work to substitutions along the aromatic backbone, post-functionalizing an aromatic polyimide. Each successive addition of an ethyl group would lead to a net gain of 2 carbons and 4 hydrogens. On the UDABAM polyimide, this would correspond to increasing hydrogen content, but at a decreasing rate as more and more substitutions take place. Figure 5, which plots the percentage of hydrogen

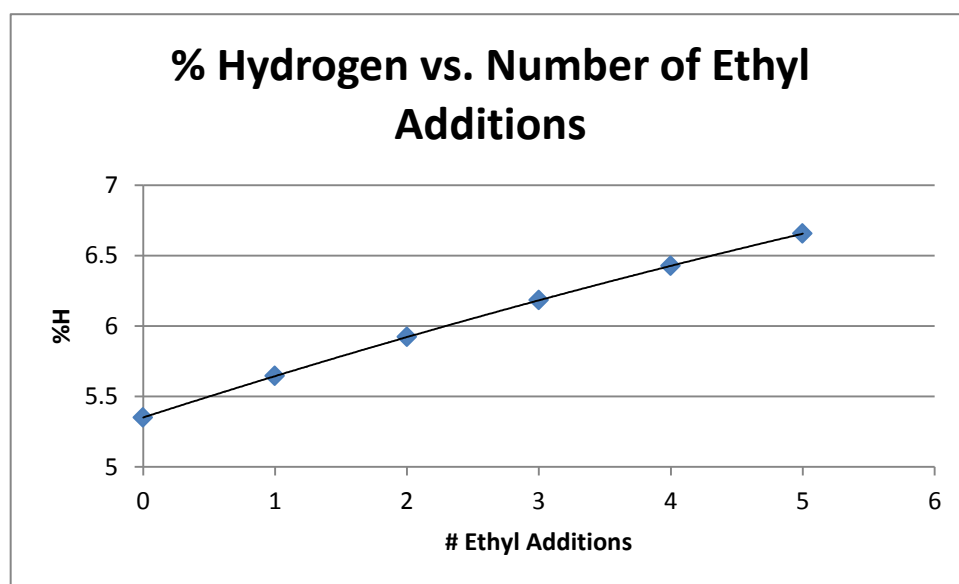


Figure 5 – % H in UDABAM vs Number of Ethyl Substituents

by mass in UDABAM as ethyl substituents are added, illustrates this trend^{*}. Each substitution also alters the regioselectivity of the system. While this might be a serious issue in the synthesis of a natural product, multiple additions would lead to further increases in the amount of hydrogen present in a polymer chain.

2. Alternative Electrophilic Aromatic Substitution

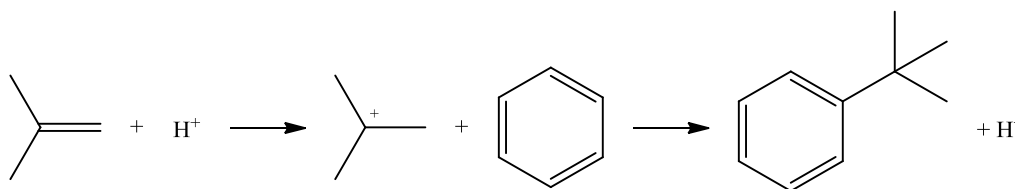


Figure 6 – Electrophilic Aromatic Addition of a t-butyl Group

Electrophilic aromatic substitutions can also be carried out by generating a carbocation from an alkene in the presence of a strong acid (Figure 6). This method involves protonating the double bond of the alkene to generate a carbocation electrophile. The carbocation then proceeds to perform the same substitution as in the Friedel-Crafts reaction via a carbocation intermediate. This process tends to be more controlled than Friedel-Crafts alkylation, and the chemicals involved are much less hazardous. When performed on an aromatic polyimide, this reaction also shows the potential for multiple additions along the repeat unit, particularly on a polymer such as UDABAM. As Figure 7 shows, t-butyl additions increase the hydrogen content of a polymer (UDABAM in this case) at a faster rate than ethyl substitutions, giving a net gain of 8 hydrogens and 4 carbons per addition. T-butyl substitutions, however, come at the price of steric hindrance, which limits the availability of certain sites along the backbone for reaction.^{*}

^{*} See Appendix for theoretical substitution positions

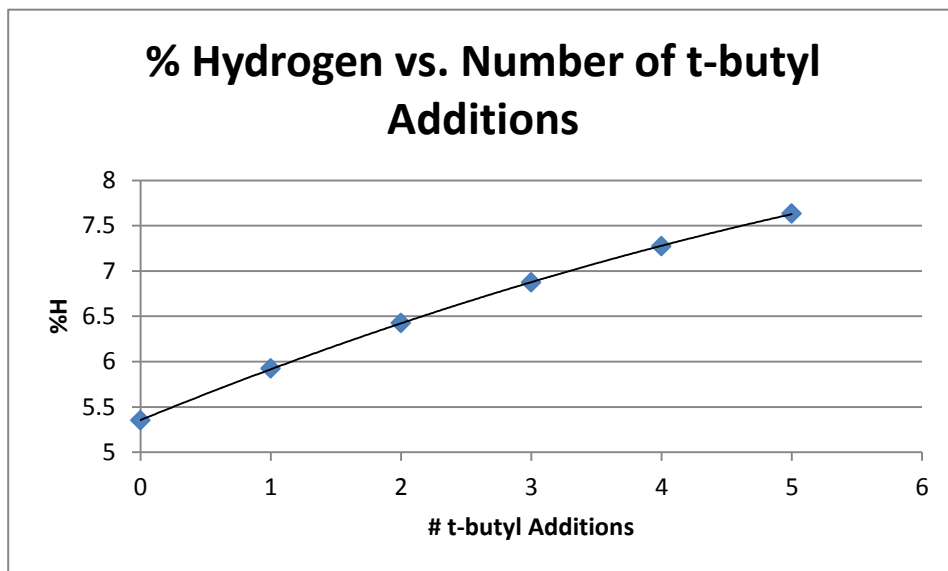


Figure 7 – % H in UDABAM vs Number of *t*-butyl Substituents

B. Crosslinking and Interpenetrating Polymer Networks (IPN)

A valuable feature of polymers is their capacity to combine the properties of two different polymers in the form of a polymer blend. Typically, polymer blending cannot be accomplished by simply mixing two polymers together. The entropy of mixing is too small to make mixing energetically favorable due to the size of the polymer molecules, so the polymer solutions will form two immiscible regions of the different materials. Chemical means must be utilized in order to mix two polymers together to create a hybrid.

One means of tailoring a polymer's properties is via crosslinking. Crosslinking is a process in which polymer chains branch out and connect with other chains, or reconnect with the same chain farther down. Crosslinking produces materials that are usually very insoluble, preferentially swelling in the presence of solvent instead of dissolving. Characteristics that determine the effect of the cross linking are cross-link density, and the average contour length between links. Crosslinking can occur as a natural side product during polymer synthesis, or it can be instigated after polymerization by linking chains together with another di-functional

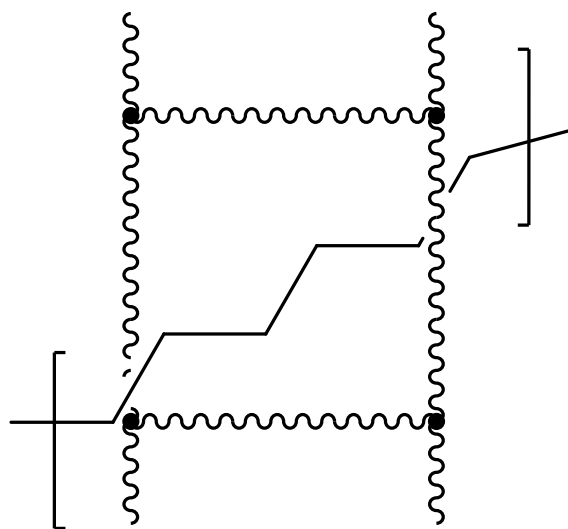


Figure 8 – Interpenetrating Polymer Network

polymer. This process allows for functional groups to be added to polymers that they could not otherwise blend with.

In addition to cross-linking, an additional technique for combining polymers in order to mix properties exists: synthesis of an interpenetrating polymer network. The idea behind an interpenetrating polymer network (Figure 8) is that chains from two different polymers are interlocked

with one another in a matrix via either physical entanglement or chemical crosslinking, thus avoiding the energetic issues associated with combining two immiscible polymers. These interpenetrating systems are not limited by the type of polymerization used to make the polymers. Chain and step growth polymers can be combined into a network, just as two chain polymers and two step polymers can be combined. There are multiple ways in which IPNs can be synthesized. A simultaneous IPN is created by polymerizing and crosslinking both polymers in the same solution at the same time. The two chains entangle one another, preventing separation. Alternatively, the two polymers can be synthesized sequentially, where one polymer has already been formed when monomer for the second polymer is added to the solution and polymerized.⁸ The second polymer forms through gaps in the first polymer creating an interwoven network. Properties of these systems can be tuned by adjusting the ratio of the two polymers present.

1. Cationic Chain Growth Polymerization

The most hydrogen-rich polymers are those that are made up of only hydrocarbons, such as polypropylene*, polyethylene*, and polyisobutylene* (each containing 14.4% H by mass). A common synthesis of these materials is cationic chain growth polymerization, which entails a carbocation propagating through carbon-carbon double bonds (Figure 9). The polymerization typically begins with a Lewis acid (metal halide) coinitiator and either a proton donor (alcohols or acids) or carbocation donor (alkyl halide) initiator. The initiator-coinitiator complex forms a cation that attacks the electron density of the carbon-carbon double bond in the monomer and a counter ion that propagates with the chain. The primary mode of termination is by

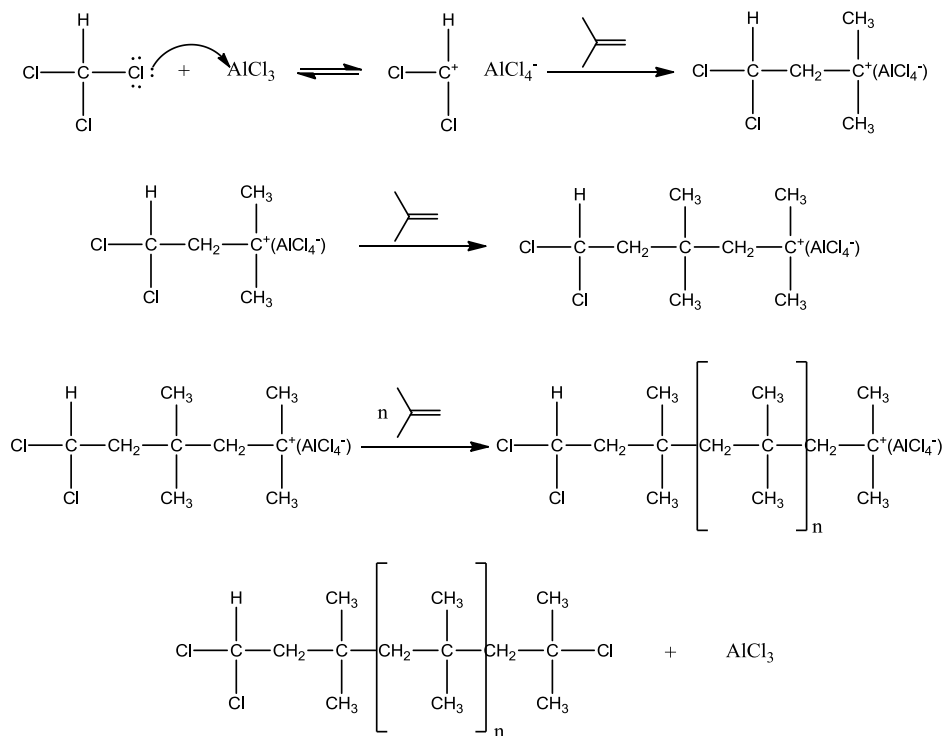


Figure 9 – Polymerization of Polyisobutylene via Cationic Polymerization

* See Appendix

recombination with the counterion. Unlike any chain transfer processes, which also terminate a growing polymer chain, termination by recombination kinetically kills the chain. This process is typically carried out in the gas phase, but it can also be performed in solution.

Solvent has a tremendous impact on the rate of polymerization and molecular weight in a cationic polymerization. Polar solvents lead to faster polymerization and increased molecular weights due to their ability to solvate the counter ion, thus reducing probability of termination by recombination. As a result, more monomer units can add to the growing polymer chain and with less hindrance before it terminates, thus potentially increasing the rate from a non-polar solvent by several orders of magnitude. In a cationic polymerization, the number average degree of polymerization (\overline{X}_n), the average number of monomers per polymer chain, is determined by the rate of polymerization, and is given by the equation:

$$\overline{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,s} + R_{tr,m}}$$

in which R_p , R_t , R_{ts} , $R_{tr,s}$, and $R_{tr,m}$ are the rates of polymerization, termination, and the three chain transfer reactions respectively.⁹ This establishes proportionality between the degree of polymerization and the rate constant of polymerization, k_p . It also shows that \overline{X}_n decreases as the rate constant of termination, k_t , increases. Applying this proportionality to the Arrhenius equation yields the following relationship (when chain transfer reactions are negligible):

$$\overline{X}_n \propto \frac{k_p}{k_t} = \frac{A_p}{A_t} e^{-(E_p - E_t)/RT}$$

Where A_p and A_t are constant, E_p and E_t are the activation energies of polymerization and termination respectively, and R is the universal gas constant. In a cationic polymerization, E_p tends to be less than E_t , which means that an increase in temperature will lead to a decrease in both \overline{X}_n and R_p . If chain transfer is non-negligible, A_t and E_t are replaced by A_{tr} and E_{tr} . E_{tr} also

tends to be greater than E_p , maintaining this relationship.⁹ Chemically, the higher temperature makes termination a more favorable process, which reduces the actively propagating chains. Consequently, reduced temperatures are much more favorable to these syntheses of high molecular weight products.

C. Aromatic Polyimides

A common feature of high-performance polymers is an aromatic or highly conjugated backbone (See Figure 3). The resonance stabilization in these bonds makes it more difficult for them to break and decompose the polymer. As a class of compounds, aromatic polyimides are very well known for their mechanical properties, making them ideal for the harsh environments necessary for space travel, and giving them the capacity to serve not only as a shield, but potentially as structural components, thus saving weight on a space craft.³ Aromatic polyimides also tend to have an excellent resistance to solvents, and a very high glass transition temperature (T_g), which is the temperature at which the polymer softens on heating from a glass to a viscous, flowing state. Although these compounds are generally amorphous, they still exhibit incredible mechanical strength and thermal resistance thanks to the conjugation in the polymer backbone. The properties of these materials can make them difficult to process, but it is not impossible. The primary limitations arise from the poor solubility and resistance to flow.

III. Experimental Methods

1-Methyl-2-pyrrolidinone (NMP, $\geq 99\%$) was purchased from Sigma Aldrich and used as received. 2-Methyl propene (isobutylene) gas (99%) was purchased from Sigma Aldrich and was condensed using a vacuum line before being used. Aluminum chloride ($AlCl_3$, extra pure, anhydrous powder, 98.5%) was purchased from Acros Organics, and was used as received.

Chloroform (>99%), methanol (>99%), ethanol (>99%) and H₂SO₄ were purchased from Fischer Scientific. Bromoethane (98%) was purchased from Alfa Aesar, and was used as received. Both high molecular weight and low molecular weight UDABAM were synthesized in house via a condensation polymerization reaction.¹⁰ The molecular weight was determined by a crease test of a film.

A. Postfunctionalization

1. Friedel-Crafts Alkylation

Friedel-Crafts alkylation reactions were attempted on UDABAM under several different conditions. 10 g (.012 mol) low molecular weight UDABAM were dissolved in 90 g (87.4 mL) NMP to create a 10 wt-% solution. 7.6 g (.06 mol) AlCl₃ were added, and smoke began evolving immediately, despite the fact that no alkyl halides had been added to the mixture. When 20 mL (.27 mol) bromoethane was added, there was no apparent evolution of gas. After 20 minutes, the solution turned white. The solution was poured into a running blender of deionized water, forcing the polymer to precipitate out of solution. The precipitated polymer was chopped into flakes by the blender. The flakes were washed with deionized water and ethanol in order to remove any residual AlCl₃ before the flakes were placed in a circulating oven at 100°C for several weeks.

Due to the vigorous reaction between the NMP and the AlCl₃, a large excess of EtBr was substituted for NMP as the solvent. This simplified the contents of the solution and added additional reagent to potentially increase the number of additions by not limiting the alkyl halide. 5 g (.006 mol) low molecular weight UDABAM was dissolved in 15 mL (.20 mol) EtBr. 2.4 g (.02 mol) AlCl₃ were then added. In order to break up the large chunk of material that formed,

20 mL of additional EtBr was added with heating (35 °C). In order to kill the reaction by neutralizing the AlCl_3 , the solution was poured into deionized water. The polymer precipitated in the beaker. The water was then poured off, and the precipitate was dissolved in NMP. The NMP solution was poured into the blender of deionized water. The flakes were then vacuum filtered, washed with water and ethanol, and placed in a circulating oven at 100°C for 10 days.

2. Electrophilic Isobutylene Addition

In order to add tertiary butyl substituents to the aromatic polymer backbone, electrophilic aromatic substitution reactions were performed based on the work of Donald Stevens on adding t-butyl substituents to cresols.¹¹ Figure 10 depicts the assembly used for this series of reactions. The reactions were performed in a three-neck flask with a



Figure 10 – Assembly Used for Isobutylene Substitution Reactions

stopper in one of the necks. The middle neck contained an overhead stirrer. A Pasteur pipette connected to a gas line that was connected to a trap with volumetric graduations fed into the third neck. The flask was suspended in a water bath to counteract the exothermic nature of the reaction. 10 g (.012 mol) of the low molecular weight UDABAM were dissolved in 60 mL (88.8 g) CHCl_3 . Approximately 7.5 g (.13 mol, 12.8 mL) isobutylene was obtained in a gas trap by pumping isobutylene gas into a vacuum line and condensing it into the trap that was cooled by liquid nitrogen. This quantity was used as a slight excess to account for gas that would bubble off and to try to force equilibrium towards the products. Four grams (2.2 mL, 3.9% by mass)

H₂SO₄ was added to the polymer solution to serve as a catalyst before the isobutylene was slowly bubbled into the solution with vigorous stirring over a period of 6 hours. This quantity of H₂SO₄ is based on the literature's use of 3-5% by weight.¹¹ The solution was stirred over night before being transferred from the three-necked flask to a rotary evaporator flask. The chloroform was then evaporated off and the flask was placed in a circulating oven at 100°C in order to remove any residual solvent. In the oven, the product changed color from a light brown to black. The product was then dissolved in excess NMP before being precipitated in a blender of deionized water. As it was being vacuum filtered, the product changed from black to light brown flakes. The product was placed in a circulating oven at 100°C for 7 days before being placed in a vacuum oven at 140°C for 7 days.

A second experiment was conducted on 5 g (.006 mol) of the low molecular weight UDABAM dissolved in 30 mL (44.4 g) CHCl₃. 2 g (1.1 mL, 3.9% by mass) H₂SO₄ were added to the solution. Upon addition of the H₂SO₄, a precipitate formed, but it redissolved over time. Approximately 6 mL (.06 mol) of isobutylene were condensed in the gas trap on the vacuum line and bubbled into the solution over 2 hours. This quantity was used based on the work of Donald Stevens that indicates a ratio of 1.8 mol isobutylene per mole of aromatic rings reduces side reactions that take place in the reaction pot.¹¹ Based on steric limitations, 4 rings per repeat unit were chosen for this calculation, which would lead to 7.2 mol isobutylene per mol UDABAM repeat units. In this experiment, that accounts for .04 mol isobutylene. The additional .02 were added to account for reagent loss. The solution was left to stir overnight. During this period, the CHCl₃ evaporated, leaving a gray clay-like slab in the flask that readily redissolved in CHCl₃. The solution, which had a black tint to it, was transferred to a rotary evaporator flask, and 15 mL deionized water was added to dilute the H₂SO₄. The solvent was evaporated yielding a white

material. When 25 mL NMP were added, the product immediately dissolved, creating a black solution. The product was precipitated in a blender of deionized water, and was vacuum filtered. It was washed numerous times with water and ethanol. The product was placed in a circulating oven in the presence of air at 100°C for 20 days before it was sent off for analysis. The final product was black, and resembled tungsten- or boron-doped polymers that are also synthesized in house.

Ten grams (.012 mol) of the low molecular weight UDABAM was dissolved in 58 mL (85.8g) CHCl_3 . 2 mL (3.7%) H_2SO_4 were added, once again yielding a small quantity of precipitate that went back into solution. Approximately 8 mL (.084 mol) isobutylene was collected using the vacuum line. This quantity was used to coincide more closely with the literature ratio, again assuming 4 reacting rings per UDABAM repeat unit. It was bubbled into the solution over a period of 4.5 hours. Ten milliliters deionized water was added to dilute the acid, then the solvent was removed using the rotary evaporator. The product was then redissolved in excess NMP, and processed using a blender prior to being vacuum filtered. During filtration, the product was washed repeatedly with water, followed by 300 mL MeOH to remove the water from the sample. The white product was placed in a vacuum oven at 140°C for 10 days before being sent off for elemental analysis.

Five grams of the high molecular weight UDABAM was dissolved in 30 mL (44.4 g) CHCl_3 . 1 mL (3.6%) H_2SO_4 was added to serve as the catalyst. Approximately 4 mL (.042 mol) isobutylene were collected in the vacuum line, and were bubbled into the solution over the course of 5 hours. This was, again, based on the same ratio of isobutylene to UDABAM that was used previously. Towards the end of the reaction, the solution's viscosity increased. This particular experiment did not utilize the water bath during the reaction. This does not appear to

have played a significant role in the reaction, as there was no noticeable temperature change and the literature suggests that this would only have an effect at approximately 70°C.¹¹ The solution was evaporated via rotary evaporator, and the product was dissolved in 70 mL of NMP at 80°C prior to being processed into flakes in a water-filled blender. The flakes were vacuum filtered and washed repeatedly with cold MeOH before being placed in a circulating oven at 100°C for 7 days before being analyzed in house.

B. Crosslinking Interpenetrating Network Synthesis

Five grams of the high molecular weight UDABAM was dissolved in 50 mL of chloroform in a beaker with stirring. Chloroform was selected as the solvent because UDABAM is soluble in it, and because chloroform and polyisobutylene have similar Hildebrand solubility parameters (19.0 MPa^{1/2} for chloroform¹² and 15.3-18.6 MPa^{1/2} for polyisobutylene¹³). Compounds with similar Hildebrand parameters can interact

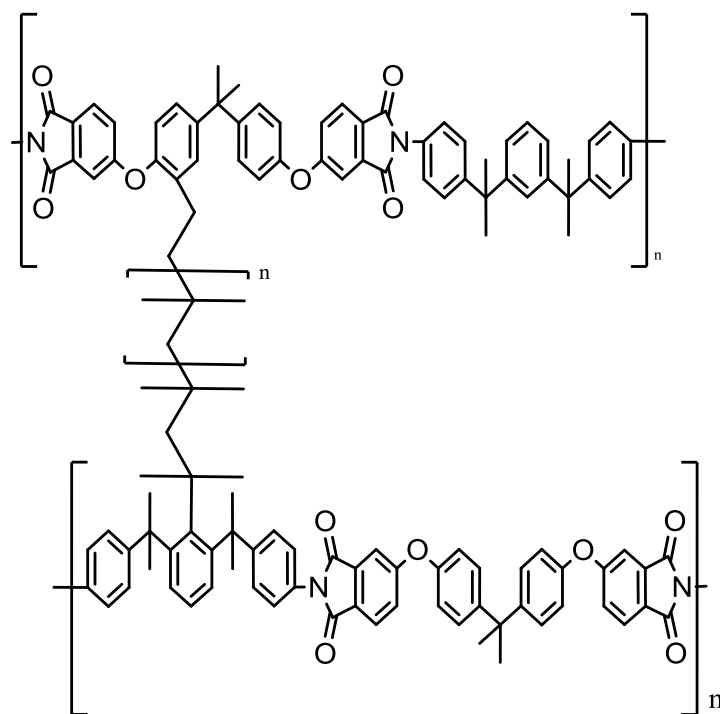


Figure 11 – Crosslinking of UDABAM Chains with Polyisobutylene linkers

via solvation, miscibility, or swelling. 1 g (.008 mol) AlCl₃ was added to serve as a co-initiator with the chloroform as the initiator in the polymerization of isobutylene monomer.

Approximately 7.5 mL (.079 mol) isobutylene was bubbled into the solution over the course of 1

hour. The isobutylene was chilled during this process, with the trap sitting in a dewar of ice. This kept the temperature low in order to increase both the rate of polymerization and the chain length. This also kept the temperature of the reagent within the literature range of -40 - 10°C for industrial production of polyisobutylene with AlCl_3 ⁹. Polyisobutylene formation was visible on the tip of the Pasteur pipette, forming long tendrils that would be periodically swept off by the stirring. The solution was left to stir overnight. During this period, the chloroform evaporated, leaving a reddish brown solid with what appeared to be distinctive layers of clear material swirled throughout.

The product was dissolved in excess NMP, forming a seemingly homogeneous solution. Over a period of several weeks, phase separation took place, producing a viscous, brown precipitate in a clear solvent that had taken on a slightly brownish tint. The beaker was heated to 125°C, which brought the material back into solution. The solution was poured into a blender of deionized water to precipitate small flakes. The flakes were vacuum filtered and washed repeatedly with water. Instead of the usually clear wash, the waste had a slightly yellowish tint. This may have been residual AlCl_3 (a yellow crystal), or material that did not come out of solution in the blender. After air filtering for several days, the majority of the flakes were placed in a circulating oven at 100°C, with a small sample being placed in a vacuum oven at 200°C.

A second synthesis was conducted on 5 g of high molecular weight UDABAM dissolved in 75 mL of chloroform in a beaker with stirring. One gram AlCl_3 was added as the co-initiator, and 4.25 mL (.045 mol) isobutylene began bubbling in slowly. Product formation was not observed on the Pasteur pipette tip, so an additional .5 g AlCl_3 was added, bringing the total amount of co-initiator to 1.5 g (.01 mol). Product formation was still not observed until the gas flow rate was increased to a rapid rate. The isobutylene was added over a period of 20 minutes,

and product formation was visible on the pipette tip. After all of the gas had bubbled into the solution, the reaction mixture stirred for three days. After this period, the solution had become dark reddish brown, and had formed a gel. The next day, the gel had hardened slightly, but still maintained its gelatinous character. A small sample (.455 g) was removed from the main gel and placed in a circulating oven at 100°C. After several days in the circulating oven, the sample was removed and reweighed at .338 g, indicating a loss of solvent. The sample was then placed in a vacuum oven at 200°C for 5 days prior to a portion being sent off for analysis.

C. Material Characterization

The elemental make-up of the Friedel-Crafts products was determined via combustion elemental analysis [C, H, N (Cl for UDABAM PIB 2)], performed by Galbraith Laboratories. For the elemental analysis data, the remaining wt-% is understood to be oxygen. The isobutylene addition products were characterized via elemental analysis, thermogravimetric analysis (TGA, for solvent retention and thermal stability), and proton nuclear magnetic resonance (^1H NMR). The ^1H NMR data was collected on a Varian 400 MHz multi-nuclear NMR instrument with deuterated chloroform as the solvent. TGA measurements were performed on a TA TGA Q500 instrument. The TGA cycle consisted of a 10°C/min ramp from 25°C to 500°C. Thermal events points were recorded. The interpenetrating polymer network products were analyzed via TGA, ^1H NMR, and elemental analysis. The TGA cycle consisted of a 10°C/min ramp from 25°C to 450°C. Again, thermal events were recorded.

IV. Results and Discussion

A. Friedel-Crafts Products

The product for the first experiment was a very fine white powder. The product for the second experiment was a white material that formed clumps with a consistency similar to a dense foam. Table 1 contains the elemental analysis data for the starting material [UDABAM (low MW)] and the two reaction products (FC UDABAM 1 and FC UDABAM 2).

Table 1			
Elemental Analysis Results for FC Products			
Sample	wt-% C	wt-% H	wt-% N
UDABAM (theoretical)	79.69	5.35	3.38
UDABAM (low MW)	76.96	5.45	3.66
FC UDABAM 1	75.10	5.24	2.97
FC UDABAM 2	77.16	5.41	3.05

Based on these results, it does not appear that the Friedel-Crafts alkylation experiments successfully post functionalized the aromatic backbone of UDABAM. A single successful ethyl substitution per repeat unit of UDABAM would have given 79.88 wt-% C, 5.65 wt-% H, and 3.27 wt-% N. The reaction products all show lower hydrogen content than the starting material, which is, in turn, lower in carbon from the theoretical starting material, but higher in nitrogen. These elemental analysis values of the reaction products leads to the conclusion that the expected Friedel-Crafts products were consistent with the starting material within experimental

uncertainty.^{*} The minor differences are most likely a result of residual NMP and water in the material. The magnitudes of differences could also be affected by differing amounts of residual solvent within each sample.

B. Isobutylene Addition Products

The first isobutylene addition reaction (t-butyl UDABAM 1) produced brown flakes. TGA analysis[†] of these flakes after drying revealed solvent (NMP) that was removed between 230°C and 325°C, and that the material began its decomposition at approximately 363°C. The ¹H NMR^{*} of this material showed no additional peaks when compared to the starting material, and the elemental analysis supported this result, indicating that the reaction did not successfully occur. The brown color was most likely a result of residual solvent during the washing process.

The second isobutylene reaction (t-butyl UDABAM 2) produced black flakes that were analyzed via elemental analysis and ¹H NMR. Again, the ¹H NMR spectrum[†] showed no differences from the spectrum of the starting material. Elemental analysis supported the conclusion that no additions had taken place. TGA analysis was not performed, as a negative result had already been established.

The third product was analyzed by TGA[†], ¹H NMR[†], and elemental analysis. The TGA revealed that by 500°C, the product had not yet reached 5% mass loss, indicating excellent thermal stability, and very little solvent was in the product. ¹H NMR, however, produced a spectrum that was identical to the starting material, and the peak integrations matched the

^{*} Based on the reproducibility in the analysis of several samples on which Galbraith Laboratories performed multiple determinations it appears that differences of up to .88 wt-% C and .38 wt-% H can be treated as experimental uncertainties. The Friedel-Crafts products were all contained within this range, indicating that they are effectively unchanged.

[†] See Appendix

amount of hydrogen for unmodified UDABAM. Elemental analysis proved very similar to the theoretical composition of the starting material.

The fourth determination, performed on high molecular weight starting materials was only analyzed by TGA* and ¹H NMR*. Once the TGA confirmed that there was no solvent in the system, the ¹H NMR analysis was performed. The peak integrations and chemical shifts matched the starting material, so elemental analysis was deemed unnecessary.

Table 2			
Elemental Analysis Results for Isobutylene Addition Products			
Sample	wt-% C	wt-% H	wt-% N
UDABAM (theoretical)	79.69	5.45	3.48
UDABAM (low MW)	76.96	5.45	3.66
t-butyl UDABAM 1	77.87	5.66	3.06
t-butyl UDABAM 2	76.28	5.18	3.17
t-butyl UDABAM 3	78.06	5.19	3.54

Table 2 contains the elemental analysis results for the first three experiments, as well as the starting material and theoretical compositions for comparison. The products all failed to show any increase in the hydrogen content of the polymer, and product 3 very closely resembles the theoretical composition of unmodified UDABAM, most likely due to successful removal of solvent. A single successful addition of a t-butyl group would yield 80.06 wt-% C, 5.92 wt-% H, and 3.17 wt-% N. This data indicates that no successful additions took place under these conditions, as the recorded values do not show significant difference in terms of experimental error.

* See Appendix

C. Interpenetrating Polymer Network Experiments

The first experiment yielded dark brown flakes. This product was analyzed by ^1H NMR and elemental analysis. The ^1H NMR spectrum^{*} showed, in addition to the spectrum of UDABAM, several small peaks at $\delta = 3.384$ ppm, 2.379 ppm, 1.261 ppm, and .859 ppm. TGA data^{*} suggests that these peaks may be a result of residual NMP in the material, which would account for approximately 10% mass loss between 157°C and 293°C. One of these peaks ($\delta = 1.261$ ppm), however, is consistent with the spectrum of polyisobutylene, which consists of two singlets at $\delta = 1.22$ ppm and $\delta = 1.55$ ppm.¹⁴ The elemental analysis results for this reaction are reported in Table 3. Despite the fact that polyisobutylene formation was observed during the reaction, elemental analysis did not indicate any within the sample. At some point in the processing, the polyisobutylene must have come out of the UDABAM system.

The second product, which formed a gel, has been analyzed via TGA^{*} and two separate elemental analyses that took place approximately 20 days from one another. The sample was kept in an oven at 200°C between the determinations, and was exposed to some air during this time. The TGA did not reveal any solvent, and seemed to show two distinct regions of mass loss: one from 260°C to 368°C, and the second from 380°C onwards. The first region most likely represents the decomposition of the polyisobutylene due to the graph's linear nature, which is uncharacteristic of solvent curves, while the second is the decomposition of UDABAM. The elemental analysis (Table 3) seems to confirm that some addition has taken place.

^{*} See Appendix

Table 3				
Elemental Analysis Results for Interpenetrating Network Products				
Sample	wt-% C	wt-% H	wt-% N	wt-% Cl
UDABAM (theoretical)	79.69	5.45	3.48	N/A
UDABAM (low MW)	76.96	5.45	3.66	N/A
UDABAM PIB 1	75.10	5.18	3.54	N/A
UDABAM PIB 2 (Test 1)	71.49	5.59	2.87	2.18
UDABAM PIB 2 (Test 2)	61.12	4.55	2.60	1.16

Although the hydrogen content has not increased by a significant margin in the second product, the ratio of hydrogen to carbon has changed in both analyses. In the theoretical polymer, the ratio $\%H / \%C = .068$. In the first test, when the carbon content is nearly 8% lower than the theoretical, the ratio $\%H / \%C = .078$. This indicates that there is more hydrogen present than there was before. In the second test results, where the $\%C$ dropped to 61.12%, $\%H / \%C = .074$, a relatively small change. The difference between the carbon content in the theoretical model and the samples indicates that there is another component to the sample than just polyisobutylene and UDABAM.

Table 4 contains the masses of elements within the sample based on the assumptions that the only sources of nitrogen and oxygen come from the unreacted UDABAM. The elemental analysis data is based on the 1.287 mg sample from test 1. The Galbraith result for the nitrogen content (0.037mg) yielded the mass of the sample that was UDABAM (1.093 mg). Applying theoretical wt-% values for carbon, nitrogen, and oxygen yielded the masses of the components

that make up UDABAM in the sample (first row of numerical values in Table 4). Applying the Galbraith results to the total sample mass gave total masses for each component (third row of numerical values in Table 4). The difference between these values and the calculated UDABAM masses gave the masses for components that are designated “extraneous.” The assumption was made that UDABAM is the only source of nitrogen and oxygen.

Table 4						
Calculated Masses of Elemental Make-up of UDABAM PIB 2						
Source	C (mg)	H (mg)	N (mg)	O (mg)	Cl (mg)	Total (mg)
UDABAM	.871	.058	.037	.127	0	1.093
Extraneous Material	.049	.014	0	0	.028	.091
Total	.920	.072	.037	.127	.028	1.184
Unidentified	0.103 mg (8.00 %)					

The elemental analysis leaves a large component of the material unaccounted for. The TGA analysis did not show residual solvent, so that is not likely the cause of this unknown quantity. A possible explanation for the void is that it is chlorine. The chlorine determination was performed nearly two weeks after the carbon-hydrogen-nitrogen determination. During that time, the material may have been exposed to atmospheric water, which could hydrate the gel. This would reduce the detected percentage of chlorine by increasing the percentages of oxygen and hydrogen. If this is the case, and the unaccounted for 8% is, in fact, chlorine, there are several potential sources within the material, each with its own implications. Because the product formed a gel, it is believed that a cross-linking reaction occurred. This synthesis of polyisobutylene leads to terminal chlorine atoms on the polymer. These terminal chlorines could then undergo a Friedel-Crafts reaction in the presence of AlCl_3 , creating cross-linked UDABAM. One of these attachment points would have an additional chlorine after binding to the UDABAM backbone. Depending on the cross-linking density, this could lead to increased chlorine content.

The second analysis of the same sample, however, indicates that this is not the source of the missing material.

A second alternative is that the solvent underwent Friedel-Crafts alkylation reactions with the solvent, depositing $-\text{CHCl}_2$ substituents along the polymer backbone. This could be verified with a ^1H NMR if the sample, which is present as a gel, could be fully dissolved. Should this prove to be the case, it could have tremendous implications. This would be a post-functionalization of the polymer backbone that would allow for further reactions to abstract the chlorines and deposit more alkyl chains, thus further increasing the hydrogen content and improving the shielding capabilities of the material. Alternatively, if the chlorines prove unreactive in this scenario, they would severely reduce the shielding ability of the polymer system by encouraging cascading radiation. Should GCR particles impact the chlorine atoms, it would lead to fragmentation and increased particle flux. Again, the lack of chlorine in the second analysis of the same samples suggests that this is not the case.

Yet another alternative explanation would be that the missing composition comes from AlCl_3 ; however this is unlikely. When the sample was removed from the beaker, AlCl_3 only made up only 1.3% of the content by mass (.0059 g). After the sample was dried to a mass of .117 g, AlCl_3 would only have made up approximately 5 % of the sample, which would make aluminum only 1% of the sample.

Oxidation of the polyisobutylene components currently presents the most likely source of the unknown component. The second analysis of the UDABAM PIB 2 sample revealed decreases in the wt-% of every component of the system, including another 10 wt-% from carbon. The %H / %C ratio, however, stays relatively constant between the two determinations. The sample seems to be thermally oxidizing. Between the two determinations, the sample was

maintained at 200°C, but was exposed to more air, which would make further oxidation between samples possible. The thermal oxidation of polyisobutylene is a documented phenomenon, leading to carbonyl formation along the backbone, and potentially causing the backbone to break.¹⁵ If the sample was exposed to more air at a high temperature, and over a longer period of time, it follows that it could more completely oxidize, leading to the observed decreases without altering the %H / %C ratio to a significant degree. The thermal oxidation process abstracts hydrogens from the backbone, replacing them with carbonyls or carboxylic acid functionalities that would lead to a slight decrease in %H / %C, which matches the observed result. Whether or not thermal oxidation is, in fact, taking place has not yet been confirmed, but FTIR analysis would reveal the presence of oxidation products.

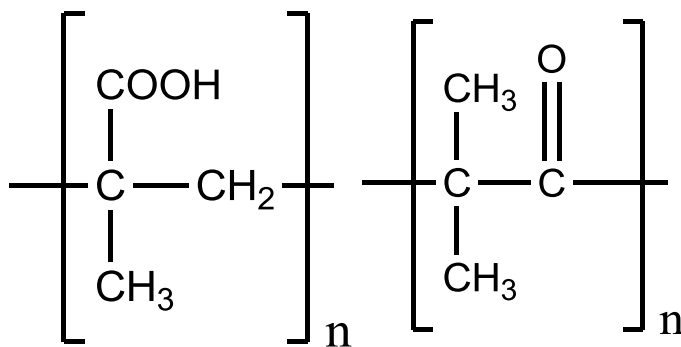


Figure 14 – Two Oxidation Products of Polyisobutylene

V. Conclusion

Radiation remains a constant threat for extended or long term and long range space exploration missions. It has the potential to cause serious harm to astronauts, including cancer and death. The equipment, especially the electronics, on a spacecraft could also suffer catastrophic damage due to the radiation. This work has attempted to develop a polymeric shield against this high energy radiation by increasing the hydrogen content of high-performance materials.

Two different techniques were attempted to increase the hydrogen content of the aromatic polyimide UDABAM by post-functionalizing the chains via electrophilic aromatic substitution reactions. Friedel-Crafts alkylation reactions with bromoethane for ethyl substituents and

aromatic substitutions for t-butyl substituents did not yield the desired increase in hydrogen content, and it is doubtful that substitution was successful. This is potentially due to the sterics surrounding the polymer chain as well as the dissociation of the charge density away from the rings in the backbone through resonance. The aromatic rings may not have been sufficiently activated for additions to take place.

A second alternative means of increasing the hydrogen content was attempted in the formation of an interpenetrating polymer network of UDABAM and polyisobutylene. This led to what appears to be a cross-linked system where polyisobutylene chains are forming the links between UDABAM chains. This experiment produced a gel that shows great promise as the basis for a shielding material. Elemental analysis revealed a much higher H/C ratio, despite the fact that the % H by mass in the sample did not increase. There remains an unaccounted for component in the system that could represent thermal oxidation of the polyisobutylene component. This product has more hydrogen in it than the starting material.

VI. Continuing Research

Further research should be devoted to additional characterization of the UDABAM PIB IPN 2 sample, as well as refinement of the synthesis process. Once the sample has been better characterized in order to determine if oxidation is taking place, the process can be optimized. The properties of interpenetrating polymer networks can be tuned by adjusting the ratios of the two polymers involved in the system.¹⁶ The interpenetrating polymer network has significant potential here for tuning the properties by adjusting the ratios of polyisobutylene to UDABAM. Reducing the temperature of the entire synthesis could also increase the hydrogen content by improving the formation of polyisobutylene and reducing the loss of monomer as unreacted gas.

Long term projects could focus on utilizing the fact that the gel could also be saturated with liquids and doped with nanoparticles in order to endow the material with additional, interchangeable properties. As the data shows, a UDABAM-polyisobutylene system could be modified to reach hydrogen contents on the level of water, if not higher with sufficient refinement. The interpenetrating network process could also be applied to several of the other novel hydrogen-rich polyimides that have been synthesized in house.

VII. References

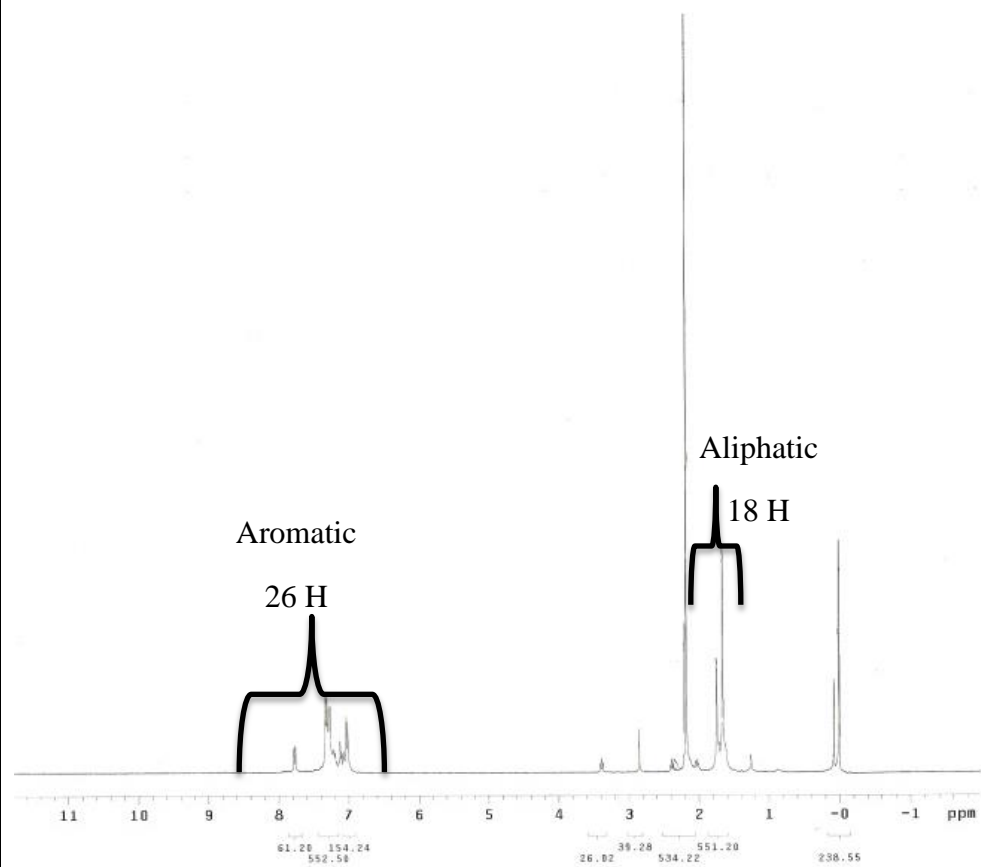
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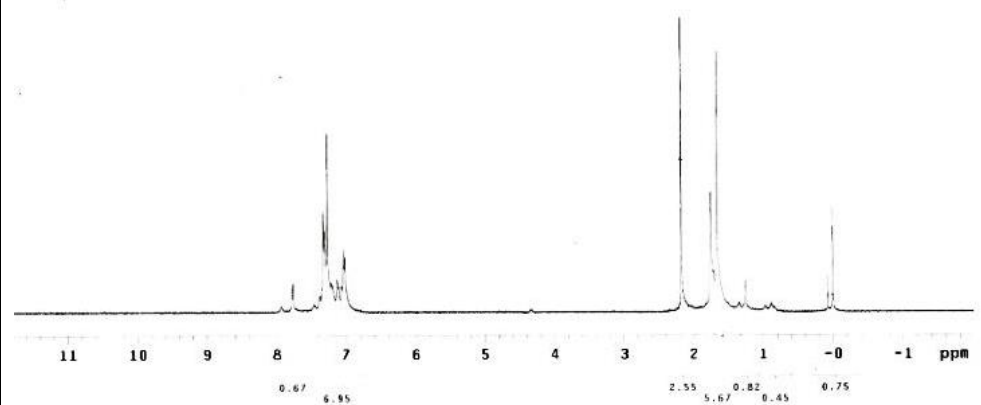
Appendix A

NMR Spectra

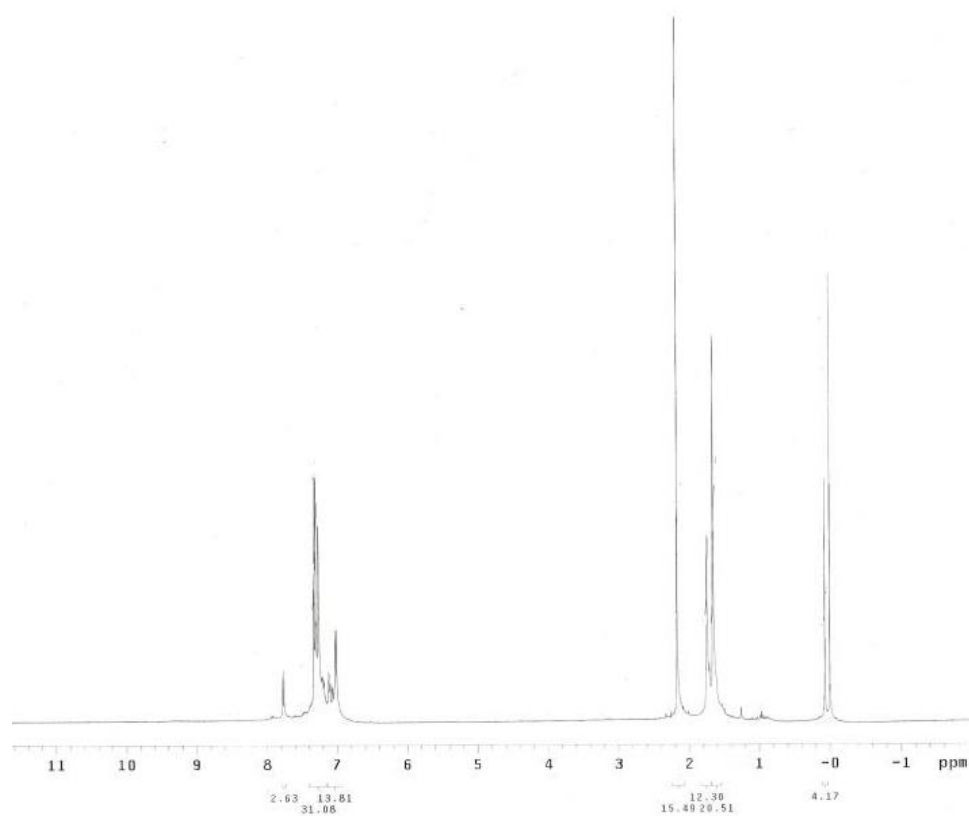
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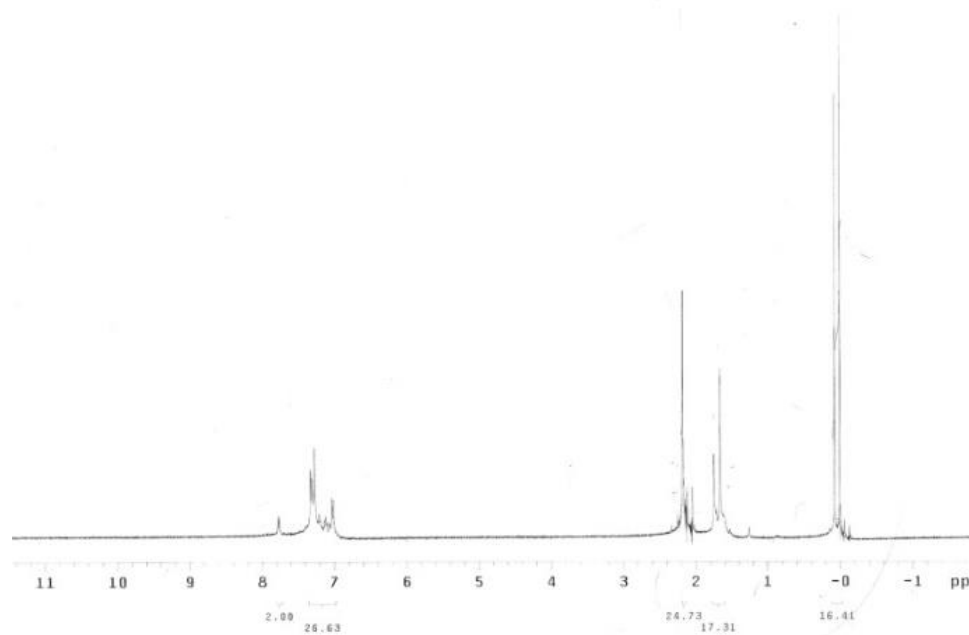
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UDABAM 1

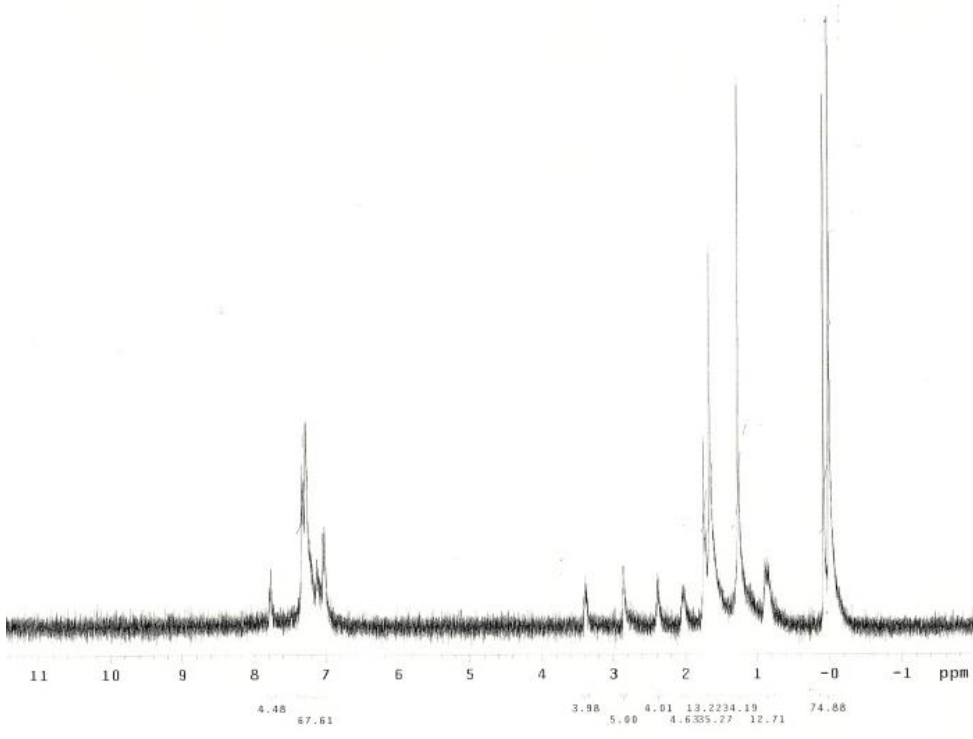


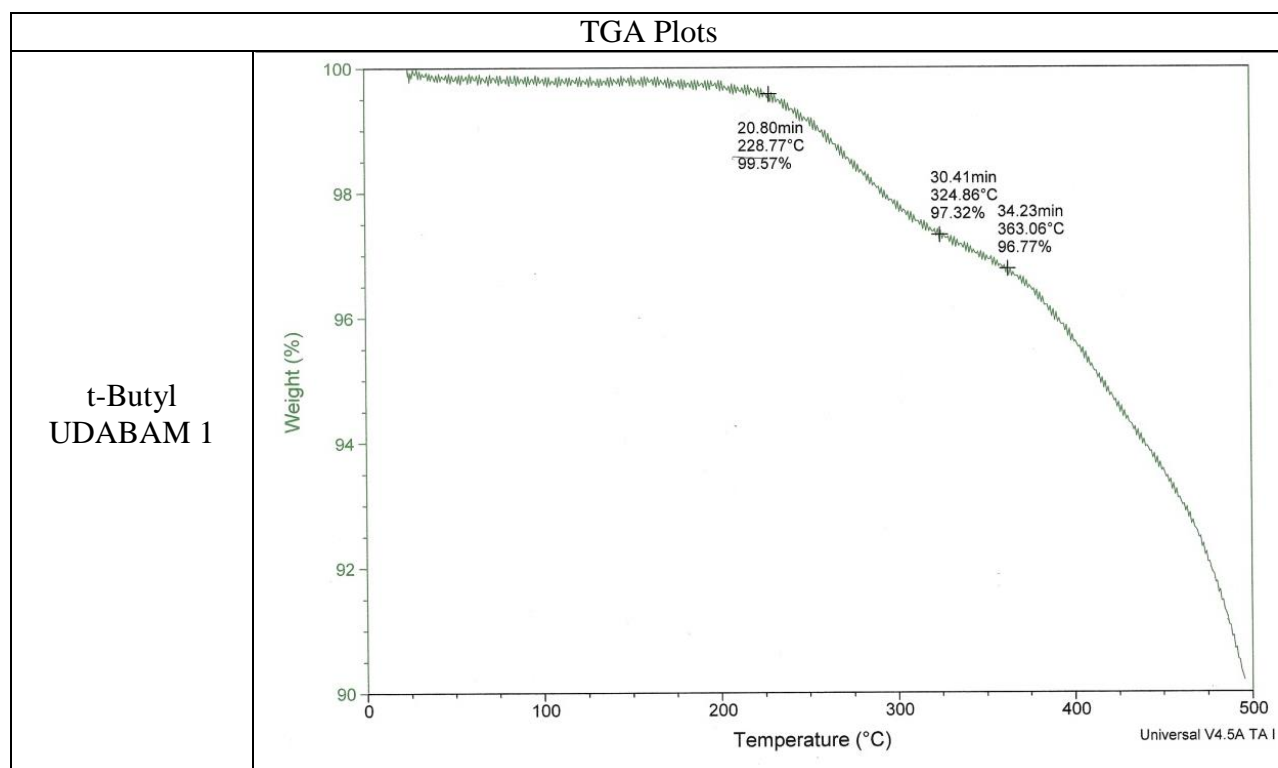
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UDABAM 2



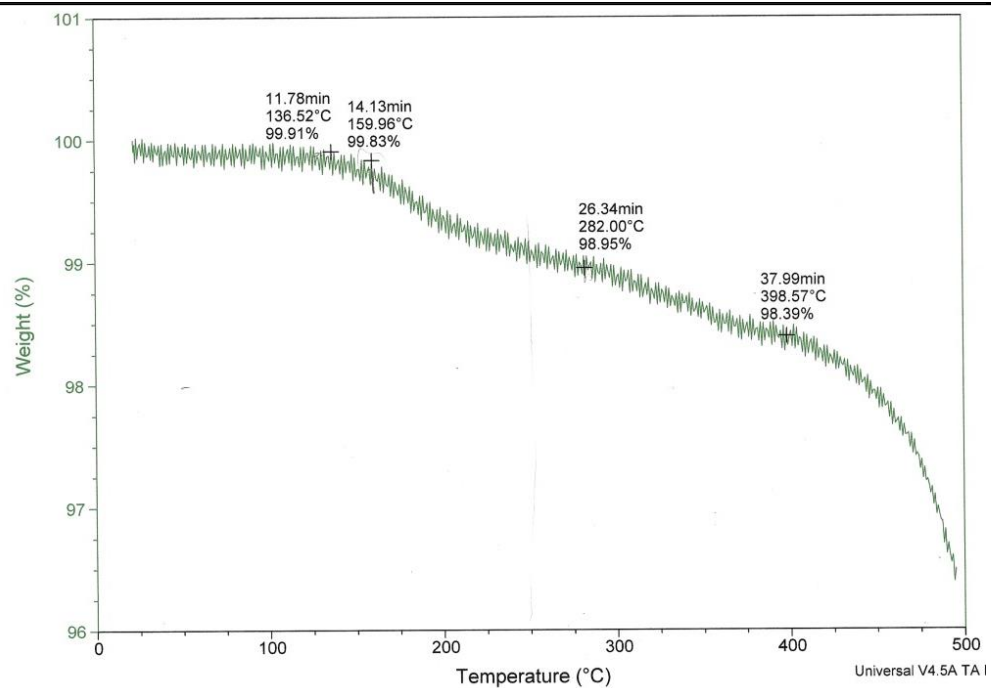
t-Butyl
UDABAM 3



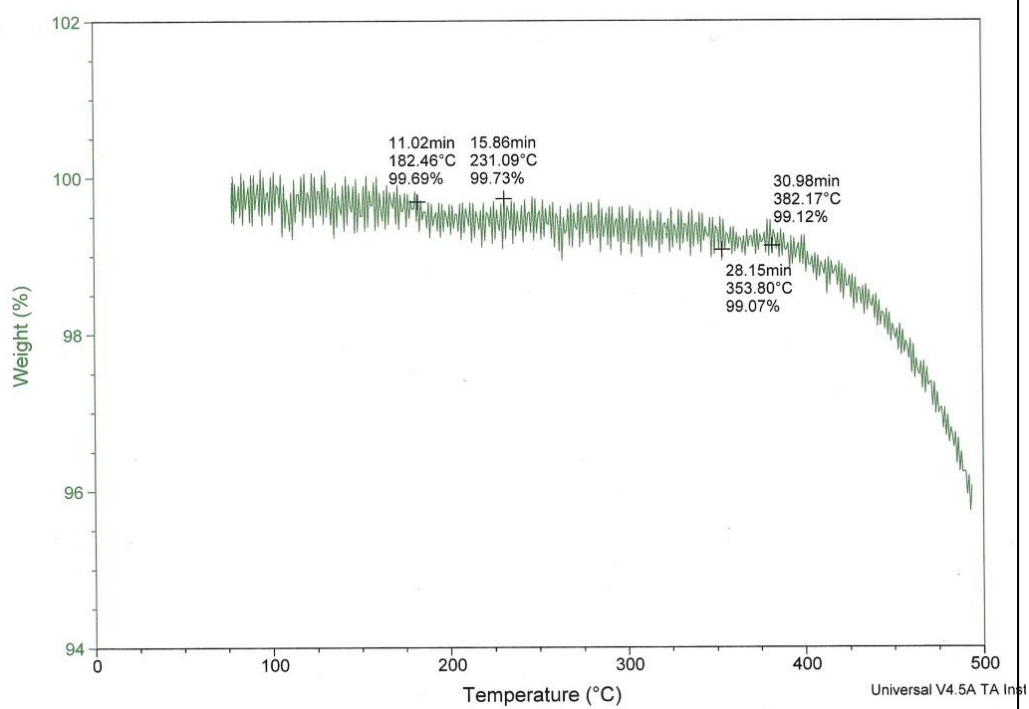
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Polyisobutylene ¹³	Singlet $\delta = 1.55$ ppm ($-\text{CH}_2-$) Singlet $\delta = 1.22$ ppm ($-\text{CH}_3$)



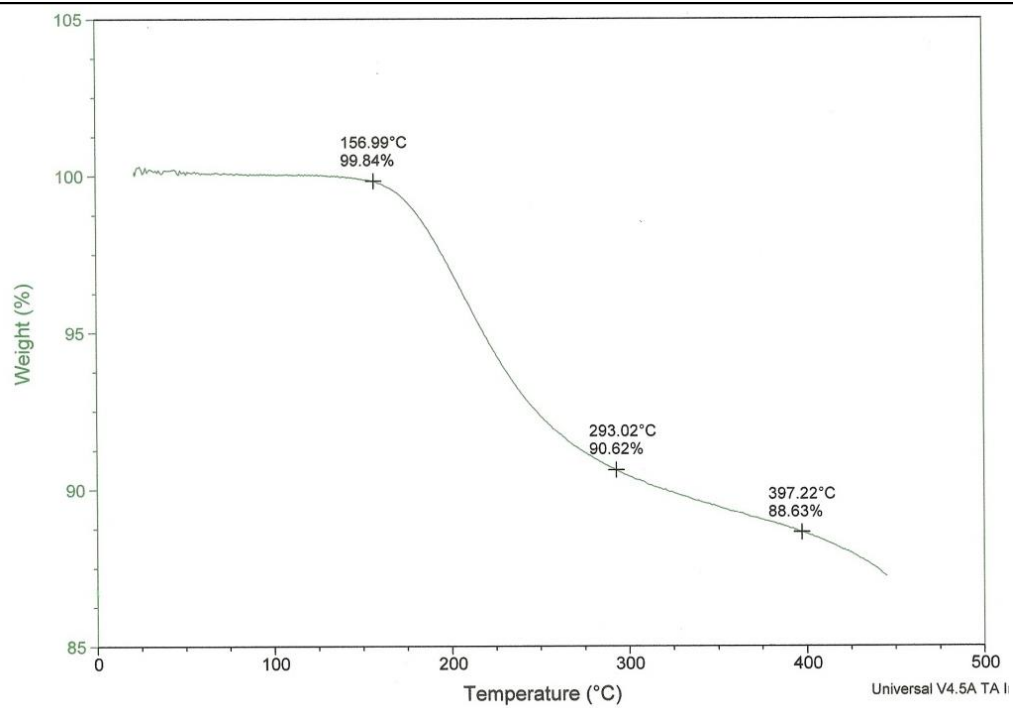
t-Butyl
UDABAM 3



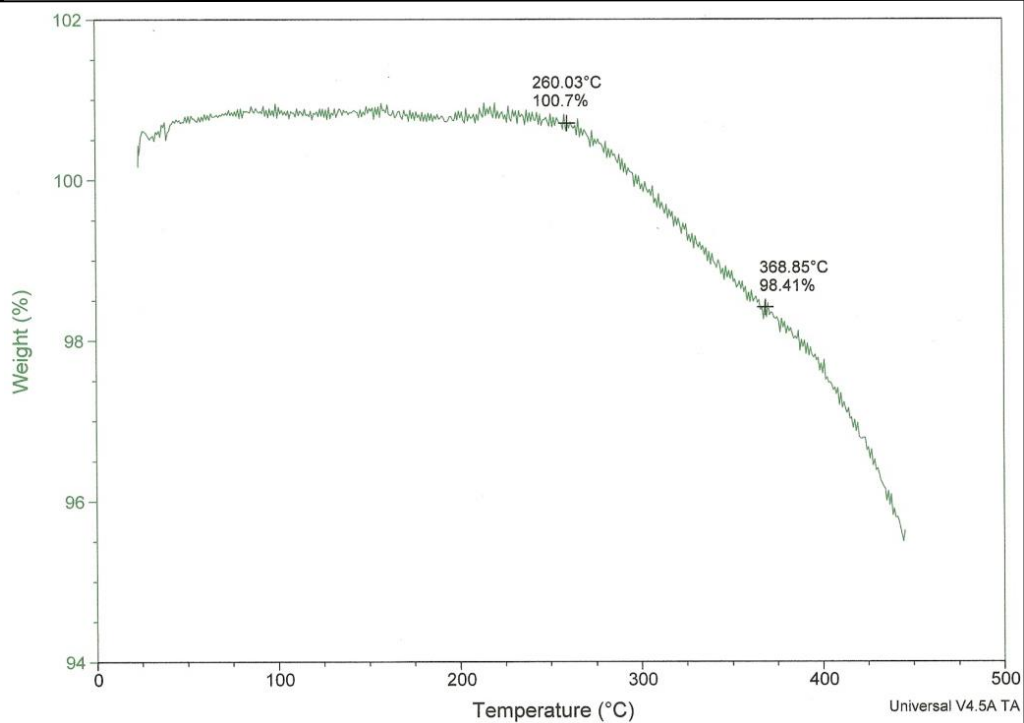
High Molecular
Weight
UDABAM

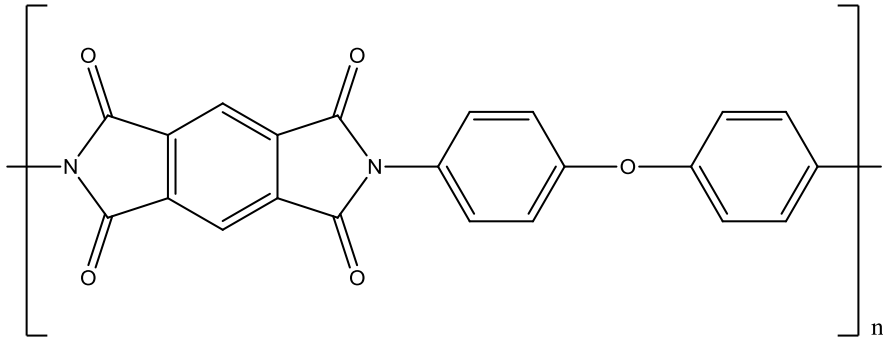


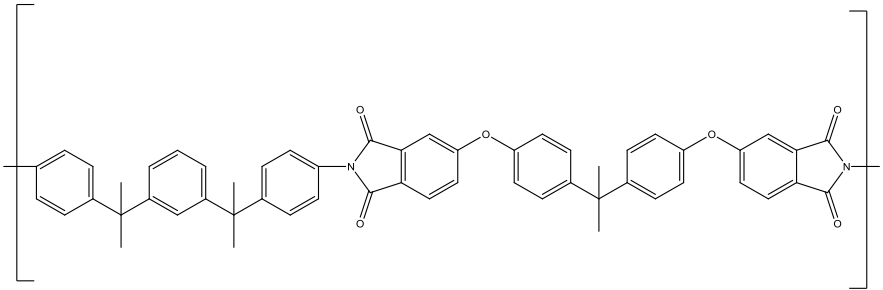
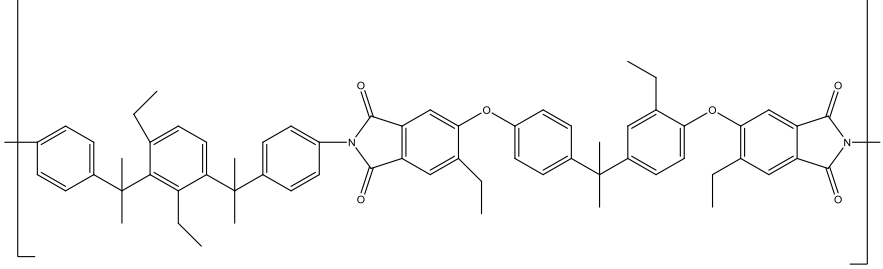
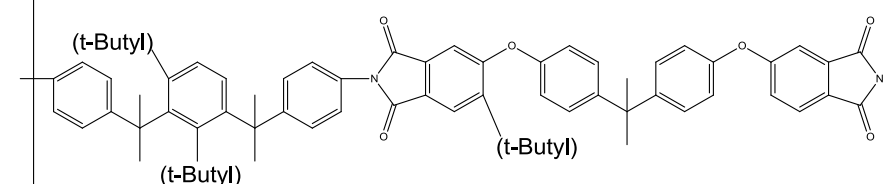
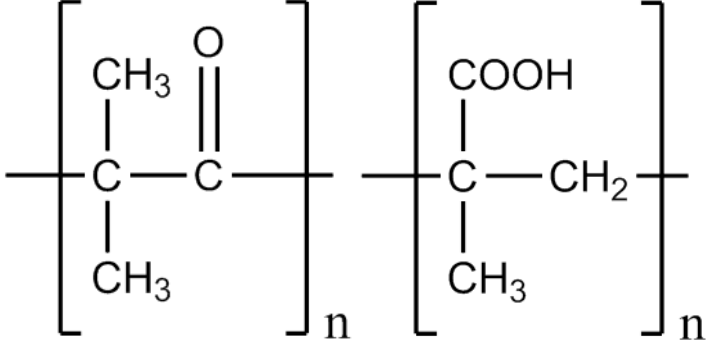
UDABAM
Polyisobutylene
IPN 1



UDABAM
Polyisobutylene
IPN 2



Polymers	
Polyethylene	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Polypropylene	$\left[\begin{array}{cc} \text{CH}_3 & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Polyisobutylene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array} \right]_n$
Kapton®	 <p>The chemical structure of Kapton® is shown within brackets with a subscript 'n'. It consists of a central benzene ring fused to two five-membered imide rings. The nitrogen atom of the left imide ring is connected to a para-phenylene ring, which is linked via an ether oxygen atom to another para-phenylene ring. The polymer backbone continues from the nitrogen of the left imide and the para position of the right phenylene ring.</p>

UDABAM	 <p>The structure shows the repeat unit of UDABAM, which is a polyimide. It consists of two 4,4'-bis(tert-butyl)phenyl groups linked by ether bonds to two phthalimide units. The phthalimide units are linked by their nitrogen atoms to form the polymer backbone. The entire unit is enclosed in brackets with a subscript 'n'.</p>
Theoretical Friedel-Craft Substitution UDABAM	 <p>This structure shows the theoretical product of Friedel-Craft substitution on UDABAM. It features the same backbone as UDABAM but with ethyl groups substituted at the 2 and 6 positions of the phenyl rings. The unit is enclosed in brackets with a subscript 'n'.</p>
Theoretical t-Butyl Substitution UDABAM	 <p>This structure shows the theoretical product of t-butyl substitution on UDABAM. It features the same backbone as UDABAM but with t-butyl groups substituted at the 2 and 6 positions of the phenyl rings. The t-butyl groups are explicitly labeled "(t-Butyl)". The unit is enclosed in brackets with a subscript 'n'.</p>
Two Oxidation Products of Polyisobutylene	 <p>This block shows two chemical structures representing oxidation products of polyisobutylene. The first structure is a polyketone, with a central carbon atom bonded to two methyl groups and a carbonyl group (C=O). The second structure is a polyacid, with a central carbon atom bonded to a methyl group and a carboxylic acid group (COOH), followed by a methylene group (CH₂). Both structures are enclosed in brackets with a subscript 'n'.</p>